Senior Thesis

Thermal Analysis: Applications in the Geological Sciences

by
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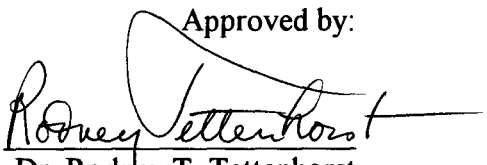

Dr. Rodney T. Tettenhorst

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Abstract

The success of thermal analytical techniques hinges upon temperature calibration. Among the methods used for calibration of temperature are magnetic transition standards, in which the loss of magnetism of a metal is measured with respect to temperature. The magnetic transition occurs abruptly at a given temperature, Tc. Previous work done by the National Institute of Standards and Technology (N.I.S.T.) displayed broad transition temperatures and large standard deviations, as was demonstrated by Gallagher et al. (1993). Through the use of simultaneous thermogravimetry/differential thermal analysis (TG/DTA) the magnetic transition of the metals may be defined more accurately. Simultaneous TG/DTA achieves better calibration by removing dependency of Tc on the heating rate. A single set of alloys and pure metals based on the Ni/Co series were used, to accurately calibrate the instrument over a significant range of temperatures. These metals range in transition temperature from approximately 358 to 1130 degrees C. Samples used in this study were obtained from Ames Labs, Ames Iowa. The homogeneity of the metals was checked by consecutive measurements of the Tc without a temperature correction. The alloys studied had the compositions; **75%Ni/25%Co**, **50%Ni/50%Co**, **25%Ni/75%Co**, as well as pure Ni and Co. ICP spectrometry was used in order to verify the compositions of the alloys, but at the time of the preparation of this paper, the analysis was not yet completed. Initial measurements of Tc are nonlinear with respect to %Co. The magnetic transitions of the alloys were more closely spaced at higher temperatures than for lower temperatures. This would lead to accurate knowledge of the furnace conditions at higher temperatures, but leave gaps for lower temperatures. In order to

separate the magnetic transition temperatures of the metals, new compositions of **80%Ni/20%Co**, **65%Ni/35%Co**, and **40%Ni/60%Co** for the alloys are proposed. These metals display sufficiently sharp magnetic transitions over a wide range of temperatures which will be useful to calibrate thermogravimetric instruments.

Introduction

Thermal analysis constitutes a set of analytical methods which trace their origin back almost 500,000 years to the first controlled use of fire by humans. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) and IUPAC define thermal analysis as "a group of techniques in which a physical property of a substance, and/or its reaction products, is measured as a function of temperature whilst the subject is subjected to a controlled temperature program" (Gallagher, 1993). A variety of techniques fall under this definition, and a detailed description of each would require an entire book. This paper will deal with those most useful in geological sciences; thermogravimetry, thermomagnetometry, differential scanning calorimetry, and differential thermal analysis. Thermogravimetry (TG) is concerned with a change in weight in response to changing temperature, or time at a constant temperature. TG by itself is not a very powerful method, but recent efforts have combined it with Fourier transform infrared spectroscopy (FTIR), mass spectrometry, and NMR techniques, making it useful for reaction and dehydration studies. Thermomagnetometry (TM) can be considered a submethod of TG. The property measured in TM is again weight change, but TM differs from TG by incorporating a constant magnetic field. TM may be used to study phase changes, reactions, and decompositions of magnetic minerals, or minerals with magnetic derivatives such as the oxidation of hematite to magnetite. Differential scanning calorimetry (DSC) measures either the heat, or the heat flux of a sample. This method is used widely to study the dehydration of minerals and the combustion of coals. Differential thermal analysis (DTA) is similar to DSC, but instead of measuring the heat associated with the sample, it

measures the temperature of the sample with respect to the furnace temperature or the temperature of an inert standard. This method may detect any changes which cause a change in the enthalpy, conductivity, or heat capacity of the sample. The modern trend is to use two analytical methods concurently, TG/TM, DTA/DSC, TG/DTA, and others. These multiple method instruments are collectively known as simultaneous instruments, and allow for more accurate knowledge of the sample temperature and furnace conditions. In order for any of these methods to be of use, the true temperature of both the furnace and the sample must be known. This is done by calibrating the furnaces with standards. Typically melting-point standards are used. A series of metals; In, Sn, Pb, etc., define the international temperature scale, and serve this purpose. A major drawback of melting-point standards, which is a result of the limited size of sample pans, is the risk of mixing or alloying metals at higher temperatures. Other problems associated with small sample pans and use of melting-point standards is that only a couple standards may be run along with the sample. A set of magnetic transition, Curie point, standards would solve these problems. The measured transition of these standards is magnetic, and they do not melt within the range of most experiments. Because of this, the sample size is increased, and the number of standards which can be run concurrently is increased. Multiple temperature ramps may be run on each sample simultaneously without fear of contamination since the standards are magnetic, and will not melt to alloy with the sample. The standards would have Curie points spaced at approximately 200 C, from 200 to 1200 C, which span the temperature range of most furnaces.

History of Thermal Analysis in Geological Sciences

True thermoanalytical techniques began in the 18th century with the acceptance of the Farenheit temperature scale. Early experiments usually utilized cooling rates instead of heating rates, as uniform, controlled heating temperature environments were not easily achieved. The main proponent of the cooling method was Frankenheim. He used thermal techniqes to analyze feldspars, amphiboles and pyroxenes. A couple years later in 1877, a Scot named Hannay used isothermal techniques to prove that gypsum was a hydrated sulfate, and not a silicate. The next important step in thermal analysis was the widespread use of the thermocouple, perfected by LeChatelier, in the late 19th century. At this time, thermal analysis was being used to explore clay minerals. Five clay minerals gave different DTA patterns, either positive or negative temperature change corresponding to exothermic or endothermic reactions, with the same programmed heat rate. Thermal analysis is still an important tool in the study of clay minerals. In the early 20th century in Japan, Honda was using a thermobalance to study gypsum. The thermobalance allowed for a sample to be heated to very high temperatures while an accurate measurement of its mass was being kept. Chlorites and serpentines were among the minerals studied by the 1920's. At this time, thermal analysis was also used to prospect for salts and iron and manganese ores. A decade later, Norton, Hendricks, and Alexander published a series of papers on the study of clays. Norton claimed that the compositions of high alumina clays could be determined within a few percent with DTA, whereas others used thermal methods as complimentary methods to direct chemical analysis and X-ray diffraction. This caused a trend away from thermal analysis in geology. In the last twenty years, thermal

methods, especially TG/TM, evolved gas analysis (EGA), and DSC, have become more common in geologic sciences. TG/TM is being used in the proximate analysis of coals. The moisture, volatile and fixed carbon contents are measured by TG, and then a magnet is added in order to determine the iron content in the ash (Charsley, 1992). EGA can be used to determine decomposition products of rocks and minerals, and it is used along with DSC in the study of water bearing minerals (Gallagher, 1993).

Experimental

Tests for homogeneity consisted of 4 heating cycles per run, each run consisting of 10 to 15 mg samples of each of the three alloys and two pure metals. These runs were performed on a TA Instruments SDT 2960 TG/DTA instrument with a niobium iron boron magnet inducing the permanent magnetic field (Figure 1).

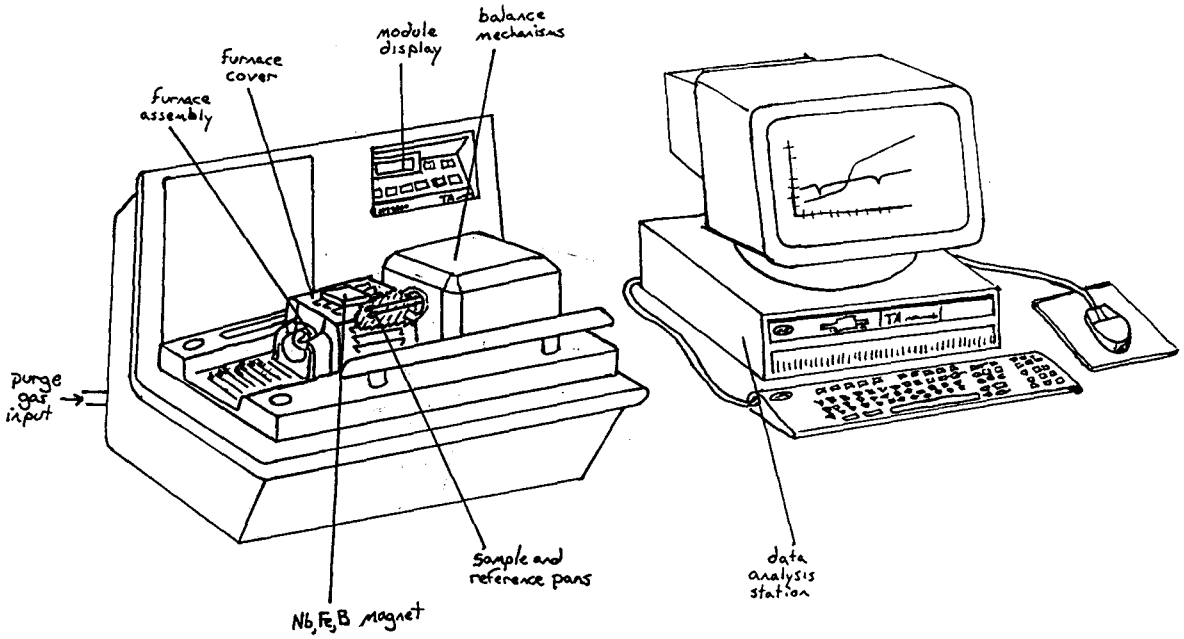

Figure 1. Schematic diagram of the TA Instruments 2960 simultaneous DTA-TGA, and Thermal Analyst 2100 data analysis system. The furnace cover is cut away to show the sample and reference pan assembly. Modifications to the original instrument include removal of a furnace cage, not shown, and use of a Nb, Fe, B magnet.

The deflection of the sample by the magnet causes an apparent high mass. The heating regime was from 200 to 1200C at 20C/min for all preliminary runs. All homogeneity tests were performed in an inert nitrogen atmosphere with a gas flow rate of 100 mL/min. This rate effectively controlled oxidation of the samples. Initial testing was performed on alloys of **75%Ni/25%Co**, **50%Ni/50%Co**, and **25%Ni/75%Co**, as well as pure nickel and cobalt (Figure 2).

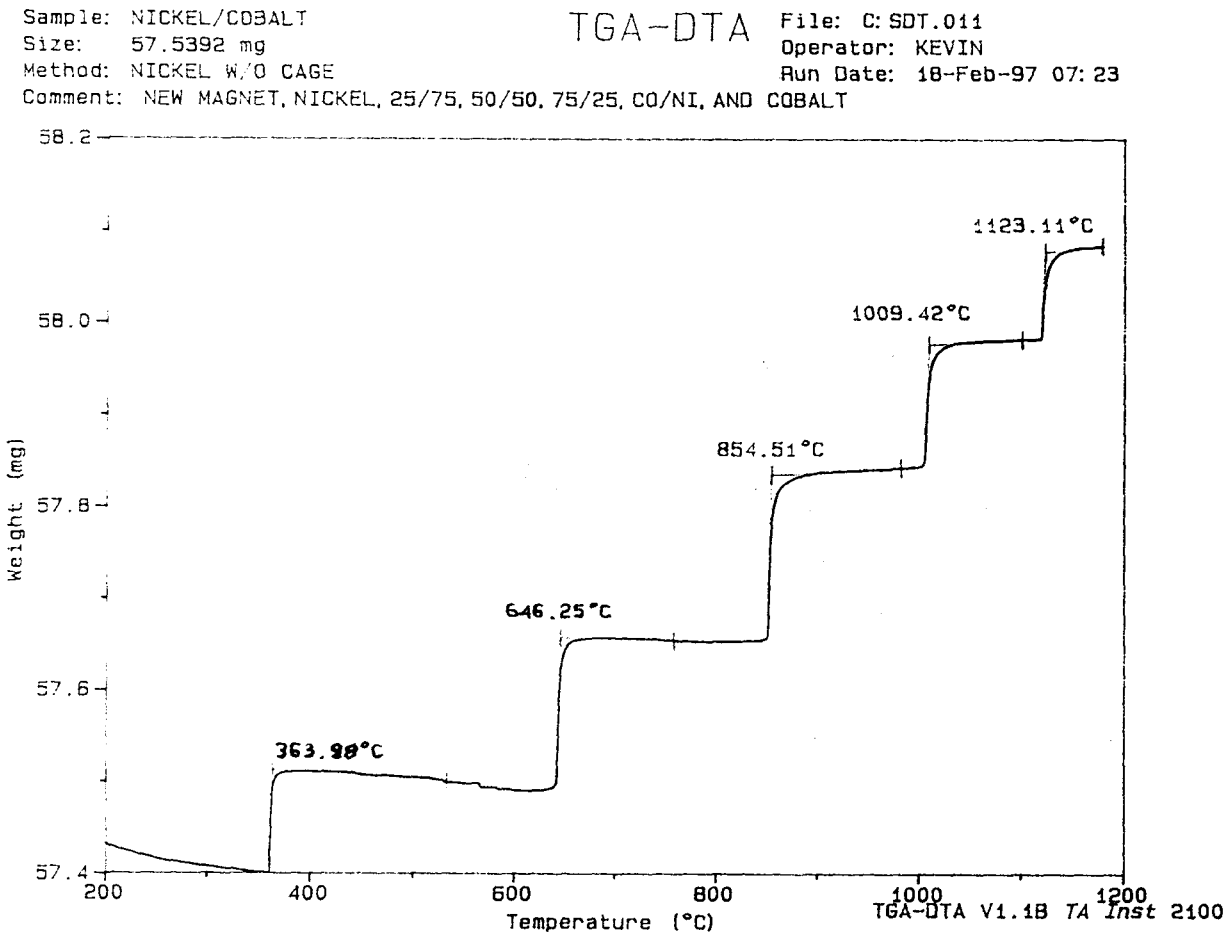

Figure 2. Sample thermomagnetometry run on Ni/Co alloys and pure nickel and cobalt. Magnetic transitions show up as apparent weight loss. The temperature at which the transition takes place, Tc, is calculated by extrapolating the weight change up to its intersection with the post-transition base line. The Curie temperatures shown are; pure Ni, 363.98C; **75%Ni/25%Co**, 646.25C; **50%Ni/50%Co**, 854.51C; **25%Ni/75%Co**, 1009.42; and pure Co, 1123.11C.

The samples had magnetic transitions which clustered at high temperatures (Table 1).

Table 1. Magnetic transition temperatures and standard deviations for six runs. Each run consists of four heating cycles on the three alloys and two pure metals (Appendix 1). Small standard deviations indicate that the alloys are homogeneous. The average Curie temperatures are used to estimate the required compositions of the new alloys (Figure 3).

Curie temperature and standard deviations for Ni,Ni/Co alloys, and Co

		nickel/cobalt alloys				
		nickel	75%/25%	50%/50%	25%/75%	cobalt
run 1	avg. of 4 ramps	363.65	646.033	855.303	1009.31	1122.61
	std. dev.	0.32527	1.02846	0.15948	0.11015	0.05
run 2	avg. of 4 ramps	363.19	646.24	854.703	1009.54	1123.46
	std. dev.	0.01414	0.29103	0.15567	0.55749	0.61655
run 3	avg. of 4 ramps	364.325	646.69	853.467	1008.34	1121.84
	std. dev.	0.30406	0.31575	0.13868	0.02646	0.06557
run 4	avg. of 4 ramps	363.325	645.763	853.193	1009.25	1121.05
	std. dev.	0.00707	0.42852	0.20306	0.19604	0.02887
run 5	avg. of 4 ramps	363.543	645.99	853.308	1008.04	1122.34
	std. dev.	0.18556	0.19545	0.1034	0.18373	0.27362
run 6	avg. of 4 ramps	364.053	644.385	853.335	1009.84	1121.61
	std. dev.	0.14154	0.20632	0.29547	0.09878	0.36682
average	avg. of 4 ramps	363.683	645.758	853.88	1009.05	1122.17
	std. dev.	0.43367	0.798	0.89551	0.72593	0.85683

The temperature data plotted against the relative concentration of cobalt in the sample yields a curve which is well described by a second degree polynomial (Figure 3).

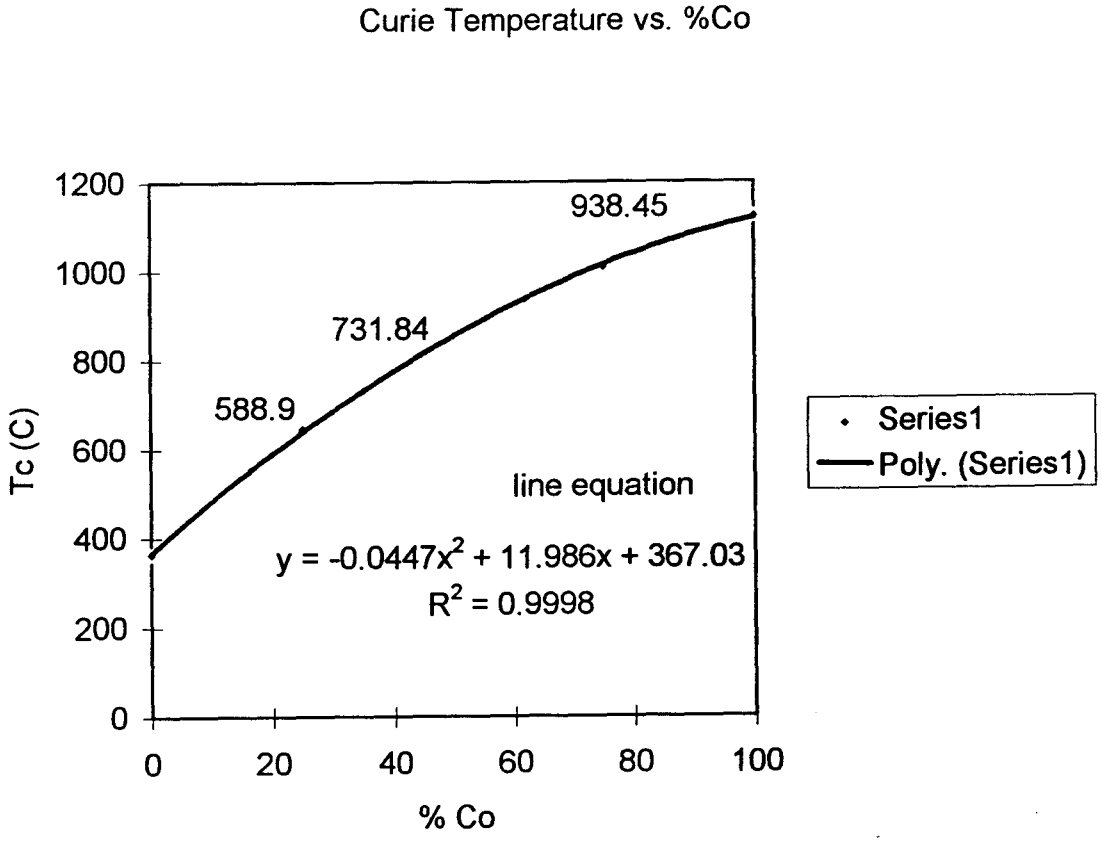

Figure 3. The Curie temperatures of nickel, **75%Ni/25%Co**, **50%Ni/50%Co**, **25%Ni/75%Co**, and Co plotted against percent cobalt in each sample. The curve displays the non-linear relationship between percent Co and the transition temperature. New sample compositions were calculated using an ideal Tc spacing of 190C, and interpolating the new percent Co for each. Compositions of **80%Ni/20%Co**, **65%Ni/35%Co**, and **38%Ni/62%Co** are calculated to give Curie temperatures of 588.90C, 731.84C, and 938.45C respectively.

By interpolating from Figure 3, a new set of sample compositions, with more evenly spaced Curie temperatures, were calculated; **80%Ni/20%Co**, **65%Ni/35%Co**, and **38%Ni/62%Co**. A low temperature alloy, **97.6%Ni/3.4%Si** was also introduced. The new samples were then analyzed. Accurate determination of the Curie temperature was performed with the same apparatus. For the standardization, a heat rate of 10C/min was used with various temperature programs. The alloys were then run individually with ICTAC approved melting point (m.p.) standards (Figure 4), which define the international temperature scale.

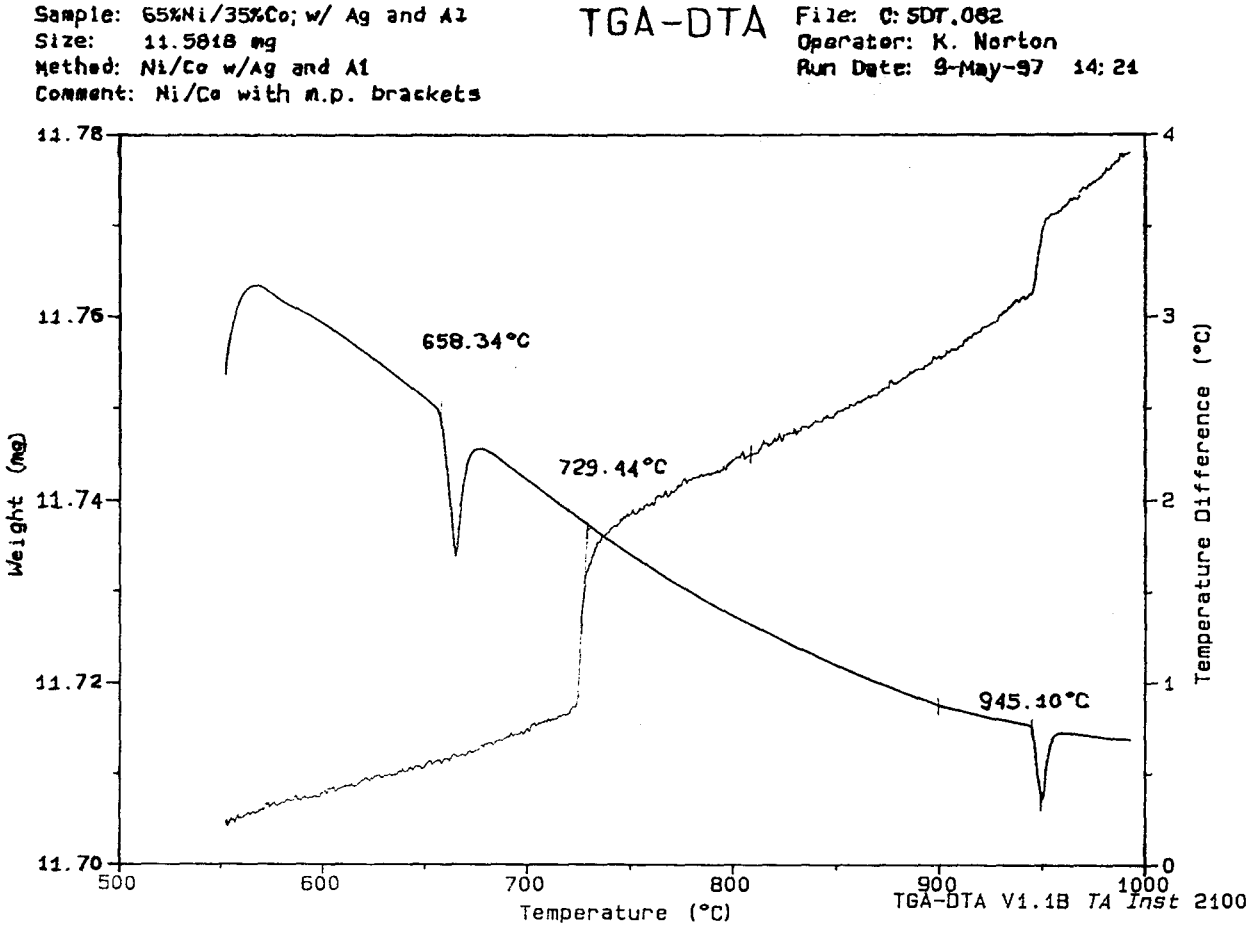

Figure 4. Sample standardization run on the **65%Ni/35%Co** alloy, Tc = 729.44C. The sample was bracketed with aluminum, m.p. = 658.34C, and silver, m.p. = 945.10C. The curve with positive slope is the TM curve for the alloy. The curve with negative slope is the DTA curve for the Al and Ag melting point standards.

The melting point standards were chosen so as to bracket the transition temperature of the alloy (Table 2).

Table 2. Experimental parameters for the standardization runs. Temperature regimes are based upon the melting points of the standards chosen. The m.p. standards were chosen that define the international temperature scale and bracket the Tc of the alloy.

Experimental Data for the Calibration of Ni/Co Alloys

	97.6%Ni/3.4%Si	80%Ni/20%Co	65%Ni/35%Co	38%Ni/62%Co
est. Tc (C)	190	588.9	731.84	938.45
temp. program	75-275C	375-700C	550-1000C	550-1150C
m.p. standards	Indium mp(C) 156.5985	Zinc mp(C) 419.527	Aluminum mp(C) 660.325	Aluminum mp(C) 660.325
	Tin mp(C) 231.928	Aluminum mp(C) 660.325	Silver mp(C) 961.78	Gold mp(C) 1064.18

Three pieces of each alloy were tested separately with four heating cycles per sample (appendix 2). This was done to insure the accurate definition of the Curie temperature of the alloy. A plot of true melting point vs. experimental melting point (figure 5) provides a calibration curve which corrects for differences between the furnace temperature and the recorded thermocouple temperature.

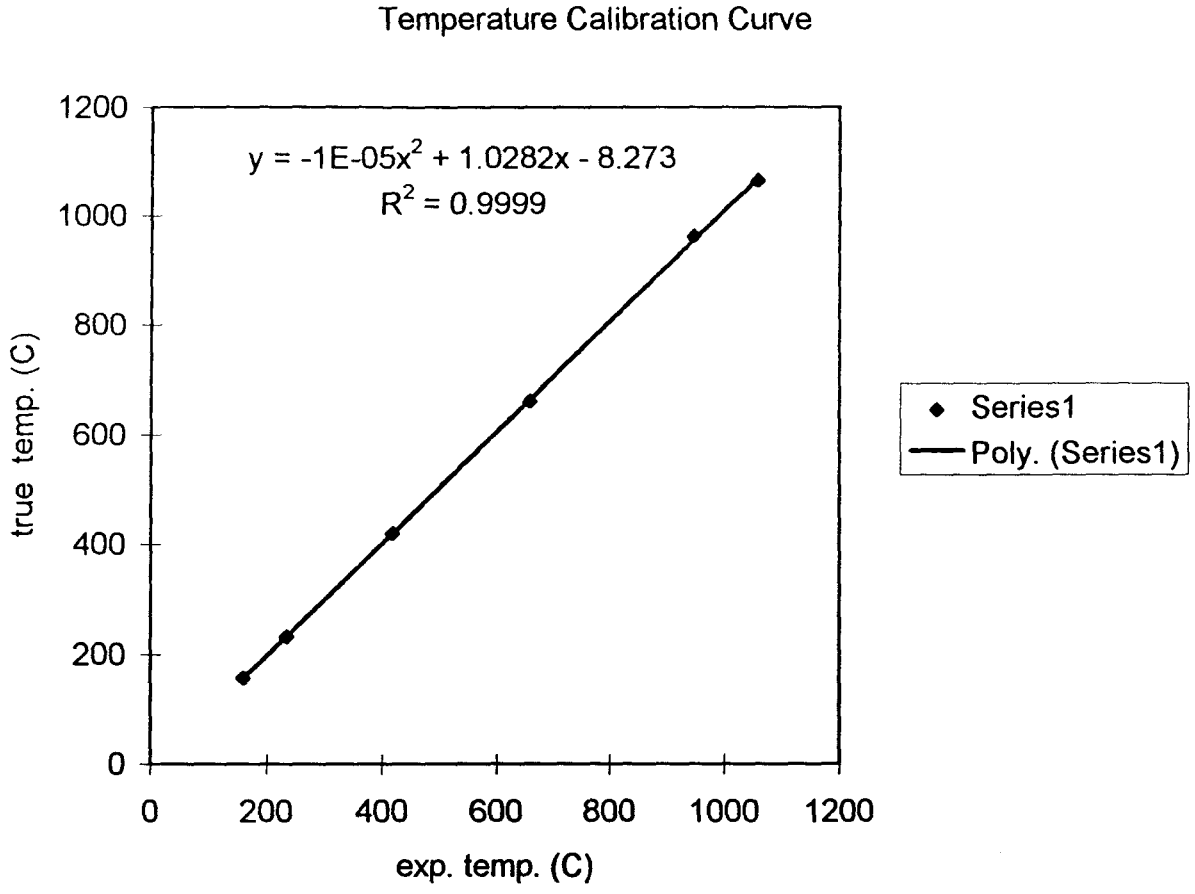

Figure 5. Calibration curve to correct experimental Curie temperatures. The true melting point of each metal is on the y-axis, and the experimental melting point is on the x-axis. The calibration accounts for any errors in the recorded sample temperature.

Conclusion

Through the use of simultaneous thermogravimetry/ differential thermal analysis, the Curie temperatures of homogeneous alloys may be accurately defined. A series of Ni/Co alloys obtained from Ames Laboratories in Ames, Iowa, were analyzed. The alloys, **80%Ni/20%Co**, **65%Ni/35%Co**, and **38%Ni/62%Co**, are homogeneous, as displayed by multiple sample analysis. The magnetic transitions of the alloys are sharp, occurring over a limited temperature range, and reproducible. The use of primary standards which define the international temperature scale allows for extremely precise determination of the Curie temperatures the Ni/Co alloys as 592.39(0.68)C, 736.20(0.08)C, and 931.58(.47)C respectively. The **97.6%Ni/3.4%Si** sample failed to display a reproducible Tc, 190.20(2.80)C, and was determined not to be homogeneous (Table 3). These alloys, when coupled with pure nickel and cobalt, which are already widely accepted TM standards, provide a set of calibration standards which span the experimental range of most experiments.

Table 3. Experimental Curie temperatures and true Curie temperatures for the melting point standards, followed by the experimentat transition temperatrues for the alloys and those calculated from calibration curves (Figure 4). Also given are the standard deviations for each alloy. Note the high standard deviation for the **97.6%Ni/3.4%Si** sample, indicating that the sample is not homogeneous.

melting point standards (C)

	exp. temp.	true temp.		exp. temp.	true temp.
In	159.6208	156.5985	Al	657.5517	660.325
Sn	234.87	231.928	Ag	945.1508	961.78
Zn	417.4683	419.527	Al	659.0433	660.325
Al	657.1931	660.325	Au	1060.336	1064.18

nickel/silicon and nickel/cobalt alloys (C)

	exp. temp.	calib. temp.		exp. temp.	calib. temp.
97.6%Ni/3.4%Si	193.1858	190.2002 (+/-2.805)	**65%Ni/35%Co**	729.9367	736.1967 (+/-0.079)
80%Ni/20%Co	589.5592	592.3883 (+/-0.676)	**38%Ni/62%Co**	927.1017	931.58 (+/-0.465)

Appendix 1

Curie Temperature Data for Homogeneity Runs

each file uses the same piece of Ni, but different pieces of the alloys and Co.

File SDT.010 3 ramps

	Ni	75/25 Ni/Co	50/50 Ni/Co	25/75 Ni/Co	Co
1st ramp		647.22	855.26	1009.26	1122.66
2nd ramp	363.88	645.48	855.48	1009.44	1122.56
3rd ramp	363.42	645.4	855.17	1009.24	1122.61
avg.	363.65	646.033333	855.303333	1009.3133	1122.61
sigma	0.3252691	1.02846163	0.15947832	0.1101514	0.05

File SDT.011 3 ramps

	Ni	75/25 Ni/Co	50/50 Ni/Co	25/75 Ni/Co	Co
1st ramp		646.46	854.85	1008.9	1124.15
2nd ramp	363.2	646.35	854.54	1009.92	1122.97
3rd ramp	363.18	645.91	854.72	1009.8	1123.25
avg	363.19	646.24	854.703333	1009.54	1123.4567
sigma	0.0141421	0.29103264	0.15567059	0.5574944	0.6165495

File SDT.012 3 ramps

	Ni	75/25 Ni/Co	50/50 Ni/Co	25/75 Ni/Co	Co
1st ramp		647.05	853.62	1008.36	1121.9
2nd ramp	364.54	646.56	853.35	1008.31	1121.85
3rd ramp	364.11	646.46	853.43	1008.35	1121.77
avg.	364.325	646.69	853.466667	1008.34	1121.84
sigma	0.3040559	0.31575307	0.13868429	0.0264575	0.0655744

File SDT.013 3 ramps

	Ni	75/25 Ni/Co	50/50 Ni/Co	25/75 Ni/Co	Co
1st ramp		646.24	852.96	1009.04	1121.03
2nd ramp	363.33	645.64	853.33	1009.43	1121.08
3rd ramp	363.32	645.41	853.29	1009.27	1121.03
avg.	363.325	645.763333	853.193333	1009.2467	1121.0467
sigma	0.0070711	0.4285246	0.20305993	0.1960442	0.0288675

Appendix 1, con't.

File SDT.014 4 ramps

	Ni	75/25 Ni/Co	50/50 Ni/Co	25/75 Ni/Co	Co
1st ramp		646.23	853.27	1007.84	1121.93
2nd ramp	363.35	646.06	853.37	1008.28	1122.48
3rd ramp	363.72	645.88	853.41	1008.05	1122.46
4th ramp	363.56	645.79	853.18	1007.98	1122.49
avg.	363.54333	645.99	853.3075	1008.0375	1122.34
sigma	0.1855622	0.1954482	0.10340052	0.1837344	0.2736177

File SDT.015 4 ramps

	Ni	75/25 Ni/Co	50/50 Ni/C0	25/75 Ni/Co	Co
1st ramp		644.68	853.4	1009.75	1121.07
2nd ramp	364.14	644.27	853.62	1009.98	1121.79
3rd ramp	364.13	644.22	853.4	1009.8	1121.87
4th ramp	363.89	644.37	852.92	1009.84	1121.72
avg.	364.05333	644.385	853.335	1009.8425	1121.6125
sigma	0.1415392	0.20631691	0.29546573	0.0987843	0.3668219

avg.	363.68306	645.758056	853.879722	1009.0476	1122.1732
sigma	0.4336696	0.79799918	0.89551377	0.7259294	0.8568263

Appendix 2

Calibration Data for Standardization Runs

97.6%Ni/3.4%Si

	TRUE	exp.	TRUE	exp.	calibrated Tc	std. dev.
In	156.5985	159.525	156.5985	159.74	190.2002	2.805224
Sn	231.928	234.92	231.928	234.7825		
97.6/3.4	192.0627	195.02	191.5642	194.5725		

TRUE	exp.	avg. exp.	slopes and intercepts of calib. curves		
156.5985	159.5975	159.6208	-2.78791	-3.75243	-3.04032
231.928	234.9075	234.87	0.999131	1.003824	1.000259
186.9739	189.965	193.1858			

80%Ni/20%Co

	TRUE	exp.	TRUE	exp.	calibrated Tc	std. dev.
Zn	419.527	417.195	419.527	417.8875	592.3883	0.079163
Al	660.325	657.0725	660.325	657.3067		
80/20	592.3752	589.3825	592.3164	589.6875		

TRUE	exp.	avg. exp.	slopes and intercepts of calib. curves		
419.527	417.3225	417.4683	0.731066	-0.76715	0.603077
660.325	657.2	657.1931	1.003837	1.005759	1.003837
592.4731	589.6075	589.5592			

65%Ni/35%Co

	TRUE	exp.	TRUE	exp.	calibrated Tc	std. dev.
Al	660.325	657.3975	660.325	656.95	736.1967	0.67615
Ag	961.78	944.91	961.78	945.2825		
65/35	736.7523	730.29	736.3938	729.7075		

TRUE	exp.	avg. exp.	slopes and intercepts of calib. curves		
660.325	658.3075	657.5517	-28.952	-26.5239	-31.2532
961.78	945.26	945.1508	1.048494	1.045512	1.05054
735.4438	729.8125	729.9367			

Appendix 2, con't.

38%Ni/62%Co

	TRUE	exp.	TRUE	exp.	calibrated Tc	std. dev.
Al	660.325	657.2625	660.325	657.4675	930.0941	0.465144
Au	1064.18	1058.785	1064.18	1057.118		
38/62	930.4426	925.82	929.5659	923.905		

TRUE	exp.	avg. exp.	slopes and intercepts of calib. curves		
660.325	662.4	659.0433	-0.75563	-4.06018	-3.96661
1064.18	1065.105	1060.336	1.005809	1.010522	1.002856
930.2737	931.58	927.1017			

References

Charsley E.L.; Warrington S.B. (1992), Thermal analysis - Techniques and Applications.,1, pgs. 231-232.

Dubrawsk J. V. (1991) - Differential scanning calorimetry and its applications to mineralogy and the geosciences. - Lecture Notes in Earth Science, 38, pgs. 16 -51.

Gallagher P.K. (1993), Advances in Analytical Geochemistry., 1, pgs. 211-257.

Gallagher P.K.; Zhong Z.M.; Charsley E.L.; Mikhail S.A.; Todoki M.; Taniguahi K.; Blaine R.L. (1993) - A study of the effect of purity on the use of nickel as a temperature standard for thermomagnetometry. - Journal of Thermal Analysis, 40(3), pgs. 1423-1430.

Haines P.J. (1995), Thermal Methods of Analysis: Principles, Applications, and Problems., 1, pgs. 1-20.

Keattch C.J. (1969), An Introduction to Thermogravimetry., pgs. 41-47.

Mackenzie R.C. (1970), Differential Thermal Analysis.,1, pgs 3- 25.

Mackenzie R.C. (1991) - Geosciences in thermal analysis development. - Lecture Notes in Earth Science, 38, pgs. 2-15.

Warne S.S.J. (1991) - Thermal analysis. A resurgence in the earth sciences: with applied, industrial and environmental aspects.-Thermochimica Acta, 192, pgs. 19-28.

Weddle B.J.; Robbins S.A.; Gallagher P.K. (1995) - Further studies on the use of TM/DTA to establish magnetic transition temperatures.- Pure Applied Chemistry, 67(11), pgs. 1843-1847.